Indian J. Phys. 77A (6), 581-586 (2003)

AN INTERNATIONAL JOURNAL
IJPA

Superconducting gap excitations in Raman spectra of CDW systems: 2H-$NbSe_2$ revisited

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Abstract : The phonon spectral function for charge density wave (CDW) system in the superconducting (SC) phase is calculated for finite wave vectors (q). An exact expression for the q dependent phonon self-energy is obtained. The analysis is carried out with $q = 0$ limit. The spectral function shows a peak for frequency ω less than the SC energy gap (2Δ) for $q = 0$. The temperature dependence of the Raman peak is discussed with variation of the electron-phonon coupling (s), superconducting gap parameter (z), temperature (t), half-width of the peak (e) and the charge density wave frequency (p). The results are discussed in context with the Raman scattering observations of SC gap excitations in 2H-$NbSe_2$ (a layered compound exhibiting both CDW and SC transitions) by Sooryakumar and Klein.

Keywords : Charge density wave superconductor, Raman spectra, electron-phonon interaction.

PACS Nos. : 71.45.Lr, 78.30.-j, 71.38.-k

1. Introduction

The charge density wave (CDW) superconductors include layered dichalcogenides of the type 2H–AM_2 [A = Nb, Ta and M = S, Se], $Nbse_3$ and the compounds with the A_{15} and C_{15} structures among others. There is much evidence to show that high T_c oxides may also belong to the group of materials as reported in the review [1]. We discuss below the competition between the instability of the Fermi surface and the superconducting gap in reference to the layered dichalcogenides.

The transition metal dichalcogenides which have hexagonal layered structures are known [2] to exhibit charge density wave (CDW) transitions. In particular, 2H-$NbSe_2$ undergoes an incommensurate CDW (ICDW) transition at $T_d = 33$ K, similar to that of 2H-$TaSe_2$ [3]. A zone center low frequency optic phonon arising from the CDW amplitude mode (CDW-AM) accompanies this transition. Furthermore, this system is a superconductor below $T_c = 7.2$ K with a Bardeen-Cooper-Schrieffer (BCS) gap $2\Delta = 17.2$ cm^{-1} as measured by infrared transmission [4]. Experiments on superconducting 2H-$NbSe_2$ have detected two ordinary Raman lines at 234 and 248 cm^{-1} [5] besides Raman lines induced by CDW below $T_d \simeq 33$ K at 40 cm^{-1} [5]. Sooryakumar and Klein (SK) [6] observed the same CDW-AM mode for the compound in both A and E symmetries near 40 cm^{-1} below the transition $T_d = 33$ K. On further cooling below superconducting transition $T_c = 7.2$ K, they observed a new gap mode (A_{1g} symmetry at 19 cm^{-1} and E_{2g} peak at 15.5 cm^{-1}) in the phonon Raman spectrum of this compound at 2 K besides the CDW-AM mode at 40 cm^{-1}. These new frequencies are close to the BCS gap $2\Delta = 17$ cm^{-1} [4]. Because the new frequency of of the new mode is close to 2Δ and application a magnetic field suppresses it [7], they concluded that the mode is due to superconducting gap excitations and becomes observable in Raman scattering through its coupling to the CDW-AM phonon.

There have been two attempts to provide microscopic theoretical explanations of the observed phenomenon and both of them assume the existence of the coupling be-

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tween the CDW-AM phonon and the superconducting electrons. The first one, due to Balseiro and Falicov (BF) [8] considers a normal electron-phonon type coupling for a single band in the phonon wave vector $q \to 0$ limit. The second, due to Littlewood and Varma [9], proposes a new mechanism of the coupling where the oscillations of the CDW amplitude produces a variation in the electronic density of states $N(0)$ at the Fermi level which in turn changes the superconducting energy gap Δ. Both the interaction mechanisms give rise to a square-root singularity at 2Δ in the phonon self-energy. This manifests itself as the observed peak in the Raman spectrum. In both the above calculations the phonon self-energy is calculated for q exactly equal to zero. In a paper Mohanty and Behera [10] considered the effect to non-magnetic impurity on the $q = 0$ gap excitation mode as observed by Sooryakumar [11]. It is important to note that only phonons with small wave vectors q contribute to the Raman scattering processes. Although the small q limit is appropriate, it should be emphasized that the extreme case of $q = 0$ does not correspond to the correct experimental situtation as pointed out by Sooryakumar and Klein [12]. Mohanty and Behera [13] evaluated the phonon self-energy in the small q limit and expalined a two peak structure for frequencies w less than the SC energy gap 2Δ in contrast to the single peak obtained by BF [8] for $q = 0$. Subsequently Behera and Mishra [14] provided a first principle derivation of the BF interaction and showd that the LV interaction can only be generated at a higher order. Klein and Dierker [15] using the BF interaction produced a detailed derivation of the collective modes of the CDW states as well as SC states and showed how these modes make their appearance in the Raman spectrum. However in all the above calculations, phonon spectral density is calculated at temperature $T = 0$ K. In this communication, we address Raman spectra at finite temperature and $q = 0$ limit.

The outline of the present report is as follows. The phonon self-energy is calculated in Section 2. The electron response function is derived in Section 3. The spectral density function is calculated in Section 4. Finallly, the results and discussions are given in Section 5.

2. Phonon self-energy for finite q

The model due to Balseiro and Falicov assumes the existence of a CDW-AM phonon which couples to the electrons in the superconducting phase *via* a normal electron-phonon type interaction. Here, we have considered CDW-phonon explicitly in the Hamiltonian. The assumption is that the phonon is the CDW phonon. The system is described by the Hamiltonian :

$$H = H_{\rm BCS} + Hp + H_{e\text{-}p}, \tag{1}$$

where

$$H_{\rm BCS} = \sum_{k\sigma} \epsilon_k C^{\dagger}_{k\sigma} C_{k\sigma}$$

$$- \Delta \sum_{k} (C^{\dagger}_{k\uparrow} C^{\dagger}_{-k\downarrow} + C_{-k\downarrow} C_{k\uparrow}), \tag{2}$$

$$H_p = \sum_{q} \omega_q b^{\dagger}_q b_q , \tag{3}$$

$$H_{e\text{-}p} = \sum_{k,q\omega} f(q) C^{\dagger}_{k+q\sigma} C_{k\sigma} A_q \tag{4}$$

and

$$A_q = b_q + b^{\dagger}_{-q}. \tag{5}$$

$C_{k\sigma}$ ($C^{\dagger}_{k\sigma}$) are the annihilation (creation) operators for electrons with momentum k and spin σ, ϵ_k is the electronic band energy, Δ is the SC energy gap parameter, b_q ($b^{\dagger}_q$) are the annihilation (creation) operators for phonons with wave vector q and energy ω_q, and $f(q)$ is the electron-phonon coupling constant assumed to be in dependent of q.

The phonon self-energy for this system is evaluated by the double-time Green's function technique [16] using the equation of motion method. The phonon Green's function is defined as

$$D_{qq'}(t-t') = \langle\langle A_q(t); A_q(t') \rangle\rangle$$

$$\equiv -i\theta(t-t') \langle [A_q(t); A_{q'}(t')] \rangle . \tag{6}$$

The equation of motion for the Fourier transformed Green's function becomes

$$D_{qq'}(\omega) = \delta_{-q,q'} D^0_q(\omega)$$

$$+ (2\pi f(q))^2 D^2_q(\omega) \chi_{qq'}(\omega) D^0_{q'}(\omega) , \tag{7}$$

where

$$D^0_q(\omega) = \frac{\omega_n}{\pi(\omega^2 - \omega^2_q)} \tag{8}$$

is the free phonon propagator and

$$\chi_{qq'}(\omega) = \sum_{k\sigma} \sum_{k'\sigma'} \langle\langle C^{\dagger}_{k-q\sigma}(t) C_{k\sigma}(t);$$

$$C^{\dagger}_{k'-q'\sigma'}(t) C_{k\sigma}(t) \rangle\rangle_{\omega} . \tag{9}$$

It is evident from (7) and (9) that the phonon self-energy

$$\sum_q(\omega) = 4\pi f^2(q)\omega_q \chi_{-q,q}(\omega) \tag{10}$$

depends on the electron response function $\chi_{qq'}(\omega)$. This quantity, when evaluated for a normal metal, gives rise to the well-known Kohn anomaly in the phonon dispersion curve. However, because we are interested in the phonon-Raman scattering in the superconducting state of 2H-$NbSe_2$, it is necessary to evaluate $\chi_{qq'}(\omega)$ with the BCS Hamiltonian (2). The equation of motion for $\chi_{qq'}(\omega)$ becomes

$$\chi_{qq'}(\omega) = \sum_{k\sigma} \Gamma(k-q,\sigma,\omega) \tag{11}$$

with $\Gamma(k-q,\sigma,\omega) = \Gamma^a(k,\omega) + \Gamma^b(k,\omega)$, where

$$\Gamma^a(k,\omega) = \left\langle\left\langle \alpha_k^a; X_{k'} \right\rangle\right\rangle_\omega ;$$

$$\Gamma^b(k,\omega) = \left\langle\left\langle \alpha_k^b; X_{k'} \right\rangle\right\rangle_\omega ; \tag{12}$$

and $\alpha_k^a = C^\dagger_{k-q\uparrow} C_{k\uparrow}$; $\alpha_k^b = C^\dagger_{k-q\downarrow} C_{k\downarrow}$;

$$X_{k'} = C^\dagger_{k'-q',\sigma'} C_{k'\sigma} . \tag{13}$$

3. Electron response function for finite q

For the calculation of the Green's function $\Gamma(k-q,\omega)$, the other higher order Green functions involving super conducting and normal states are defined as

$$\Gamma_1^a(k,\omega) = \left\langle\left\langle \gamma_k^1; X_{k'} \right\rangle\right\rangle ;$$

$$\Gamma_1^b(k,\omega) = \left\langle\left\langle \gamma_k^2; X_{k'} \right\rangle\right\rangle ; \tag{14}$$

$$\Gamma_2^a(-k+q,\omega) = \left\langle\left\langle \gamma_{-k+q}^1; X_{k'} \right\rangle\right\rangle_\omega ;$$

$$\Gamma_2^b(-k+q,\omega) = \left\langle\left\langle \gamma_{-k+q}^2; X_{k'} \right\rangle\right\rangle_\omega ; \tag{15}$$

$$\Gamma_3^a(-k+q,\omega) = \left\langle\left\langle \alpha_{-k+q}^a; X_{k'} \right\rangle\right\rangle_\omega ;$$

$$\Gamma_3^b(-k+q,\omega) = \left\langle\left\langle \alpha_{-k+q}^b; X_{k'} \right\rangle\right\rangle_\omega ; \tag{16}$$

where

$$\gamma_k^1 = C^\dagger_{k-q\uparrow} C^\dagger_{-k\downarrow} ; \quad \gamma_k^2 = C_{-k+q\downarrow} C_{k\uparrow} ;$$

$$\gamma_{-k+q}^2 = C^\dagger_{-k\uparrow} C^\dagger_{k-q\downarrow} ; \quad \gamma_{-k+q}^2 = C_{k\uparrow} C_{-k+q\uparrow} . \tag{17}$$

The new Green's functions are related as

$$\Gamma_1(k,\omega) = \Gamma_1^a(k,\omega) - \Gamma_1^b(k,\omega) ,$$

$$\Gamma_2(-k+q,\omega) = \Gamma_2^a(-k+q,\omega) - \Gamma_2^b(-k+q,\omega) \tag{18}$$

The electron response function in the limit $q \neq 0$ at finite temperature is calculated from the Green's function given in eqs. (14) to (18).

$$\chi_{qq}(\omega) = \chi_{qq\uparrow} + \chi_{qq\downarrow}$$

$$= \frac{1}{2\pi}\sum_k \frac{1}{|D|}\Big[\left(\omega^2 - \epsilon_+^2(k,q)\right)\left(\omega - \epsilon_-(k,q)\right)$$

$$\times (n_{k-q} - n_k) + 4\omega\Delta(\omega - \epsilon_-(k,q))(\phi_{k-q} + \phi_k)\Big] \tag{19}$$

with $n_{k-q} = (n_{k-q\uparrow} + n_{k-q\downarrow})$,

$$|D| = (\omega^2 - E_+^2(k,q))(\omega^2 - E_-^2(k,q)) \tag{20}$$

where $E_\pm(k,q) = E_{k-q} \pm E_k$, $\epsilon_\pm(k,q) = \epsilon_{k-q} \pm \epsilon_k$ and $E_{k-q}^2 = \epsilon_{k-q}^2 + \Delta^2$ is the energy of the superconducting excitation.

The Fermi function $n(k-q)$ and superconducting amplitude ϕ_{k-q} are given by

$$n_{k-} \qquad \frac{\epsilon_{k-q}}{E_{k-q}} \tan h\left(\frac{\beta E_{k-q}}{} \right. \tag{21}$$

and

$$\phi_{k-q} = \left\langle C^\dagger_{k-q\uparrow} C^\dagger_{-k+q\downarrow} \right\rangle$$

$$= \frac{\Delta}{2E_{k-q}} \tan h\left(\frac{\beta E_{k-q}}{2}\right. \tag{22}$$

The weak coupling BCS gap parameter is

$$\Delta = -\sum_k \tilde{V}_k \left\langle C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} \right\rangle \tag{23}$$

and ten superconducting gap equation reduces to

$$1 = g\int_{-\omega D}^{\omega D} d\epsilon_k \left| \frac{\Delta}{2E_k} \tan h\left(\frac{\beta E_k}{2}\right. \right| . \tag{24}$$

$g = N(0)V_0$ is the superconducting coupling constant with $N(0)$ the electron density of state at the Fermi level and V_0 the effective coulomb interaction.

4. Raman Spectra in the limit $q = 0$ and finite T

The phonon spectral density function (SDF) in the limit of $q = 0$ and finite temperature T is given by

$$S(\omega, q = 0) = -\pi I_m D_{qq}(\omega)|_{q=0} . \tag{25}$$

The SDF, which is measured in Raman scattering, can be calculated by attributing a finite width (η) to the phonon

$(\omega^2 \rightarrow \omega^2 + 2i\eta)$. In $q = 0$ limit and at finite temperature T, the SDF is calculated from eq. (25) by using the Green's function $D_{qq}(\omega)$ from eq. (7) and response function from eq. (19). The SDF is given by

$$S(\omega, q=0) = \frac{\omega_0 B_1}{A_1^2 + B_1^2}, \tag{26}$$

where $A_1 = \omega^2 - \omega_0^2 - A$

and

$$B_1 = 2\eta\omega - B \tag{27}$$

with $A = 8\omega_0^2 s \int d\epsilon_k \, I^r$

and

$$B = 8\omega_0^2 s \int d\epsilon_k \, I^i, \tag{28}$$

where

$$I^r = \left[\frac{\Delta^2(\omega^2 - 4E_k^2)}{E_k D_0(\omega)} \tanh\left(\frac{\beta E_k}{2}\right)\right], \tag{29}$$

$$I^i = \left[\frac{2\eta\omega\Delta^2}{E_k D_0} \tanh\left(\frac{\beta E_k}{2}\right)\right]. \tag{30}$$

$$D_0(\omega) = [\omega^2 - 4E_k^2)^2 + 4\eta^2\omega^2] \tag{31}$$

and

$$E_k = (\epsilon_k^2 + \Delta^2)^{1/2}. \tag{32}$$

The eq. (26) is evaluated by varying the model parameters which scaled by dedve energy ω_D. The dimensionless parameters are

$$s = \frac{f^2(0)N(0)}{\omega_D}, \; g = N(0)V_0, \quad z = \frac{\Delta}{\omega_D}, \; t = \frac{k_B T}{\omega_D},$$

$$e = \frac{\eta}{\omega_D}, \quad p = \frac{\omega_0}{\omega_D}, \quad c = \frac{\omega}{\omega_D}, \quad \tilde{\omega} = \frac{\omega}{\omega_0}.$$

5. Results and discussion

The different dimensionless parameters involved in the numerical calculations are the superconducting coupling strenght g, phonon coupling s, superconducting order parameter z, renormalized phonon frequency c, charge density wave frequency p, reduced phonon frequency $\tilde{\omega}$. The above phonon parameters and the electron parameters of the atomic sub-system are varied to find out superconducting excitations in Raman spectra. The temperature dependence of the BCS gap parameter is evaluated numerically and self consistently. The temperature dependence of the superconducting (SC) order parameter z is shown if

Figure 1. The SC transition temperature $t_c = 0.04$ corresponding to the $T_c = 7.2$ K for the CDW superconductor.

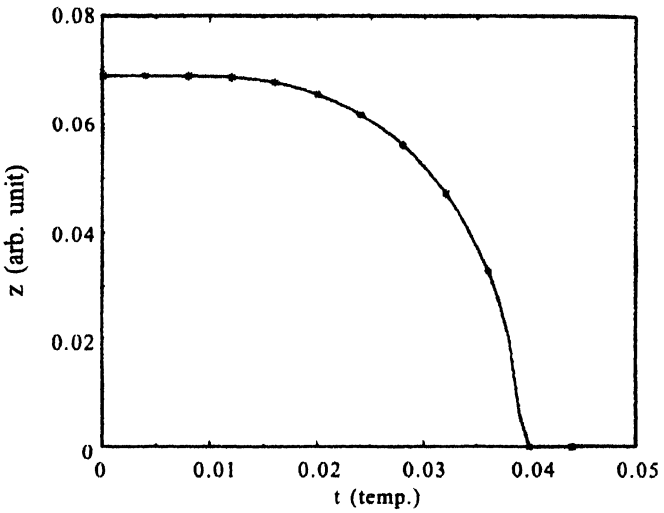

Figure 1. Plot of z *vs* t for $g = 0.297$.

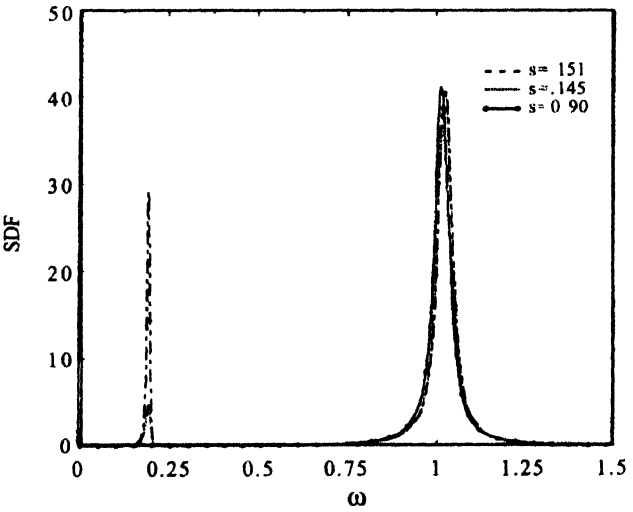

Figure 2. Plot of the spectral density function (SDF) for fixed values of $z = 0.05214$, $e = 0.012$, $p = 0.5$ and $t = 0.03$ and for different values of $s = 0.151$, 0.145, 0.09.

The gap at $T = 0$ K is $z(0) = 0.0686$ as scaled by the Debye energy $\omega_D \simeq 175$ K.

As mentioned in Section 4 we have used the value of the effective electron-phonon coupling strength parameter $s = 0.151$ for numerical calcualtion. This choice of s is dicatated by the requirements that (i) the SC gap excitation mode should have the observed experimental frequency of 17 cm^{-1} appropriate for the system ($2HNbSe_2$). We have used value of the superconducting gap $z \simeq 0.052124$ corresponding to $t = 0.03 < t_c$ as shown in Figure 1. The results of the numerical calcualtion of the spectral density func-

tion (SDF) with the above choice of parameters are presented in Figures 2 to 6. Figure 2 depicts the SC gap excitation mode for the various values of the effective electron-phonon coupling s. It can be seen from Figure 2 that the SC gap excitation appears at $\tilde{\omega} \simeq 0.195$, which corresponds $2z = c = \tilde{\omega}p = 0.0975$. Hence, the SC gap at $t = 0.03$ in the CDW phase comes at to be 0.04975 (smaller than its normal gap value $z = 0.052124$). Hence, the CDW

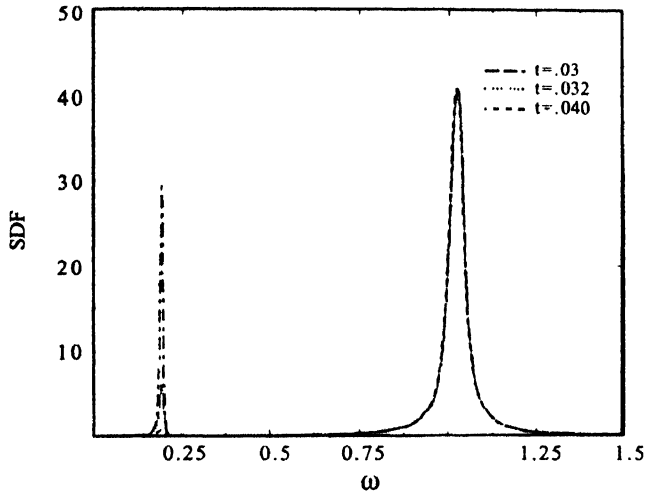

Figure 3. Plot of SDF for fixed values of $s = 0.151$, $z = 0.052124$, $e = 0.012$ and $p = 0.5$ and for different values of $t = 0.03$, 0.032, 0.04.

phase suppresses the SC gap mode towards the low frequecy as shown by expt. [6,7] and the oretical calculation [8,13]. On further decreasing s the peak shows a spectral broadening with a rapid decrease in the spectral height. For a cut off elctron-phonon coupling $s_c \simeq 01.0$, the SC gap excitation. However, the SC peak is shifted to the higher frequencies with increase of s accompanied sharp rise in peak height.

The temperature dependence of the SC gap excitaion mode is shown in Figure 3. At lower temperatures the SC gap mode at $\tilde{\omega} \simeq 0.195$ becomes sharper with decrease in spectral width but no change in frequency. However the peak show a large broadening with rapid decrease in the spectral height. At higher temperature the SC gap excitation completely disappears at $t_c = 0.042$ which is large than the temperature $t = 0.03$ corresponding to the SC gap $z = 0.052124$ (see Figure 1). This $t_c = 0.042$ is the SC transition temperature in the CDW phase, at which the SC is just coupled to the CDW phonon mode.

The effect of changing the SC gap at a fixed temperature is shown in Figure 4. As the SC gap is reduced from

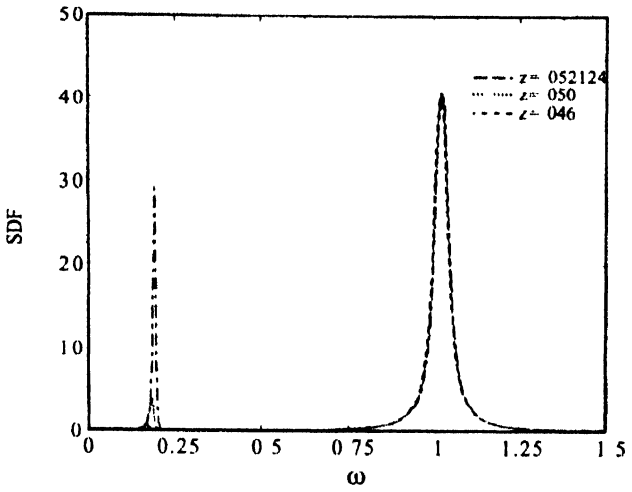

Figure 4. Plot of SDF for fixed values of $s = 0.151$, $e = 0.012$, $p = 0.5$ and $t = 0.03$ and for different values of $z = 0.052124$, 0.05, 0.046.

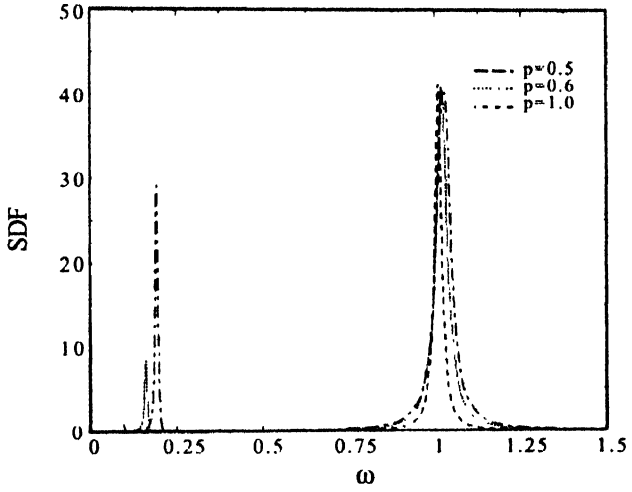

Figure 5. Plot of SDF for fixed values of $s = 0.151$, $z = 0.052124$, $e = 0.012$ and $t = 0.03$ for different values of $p = 0.5$, 0.6, 1.0.

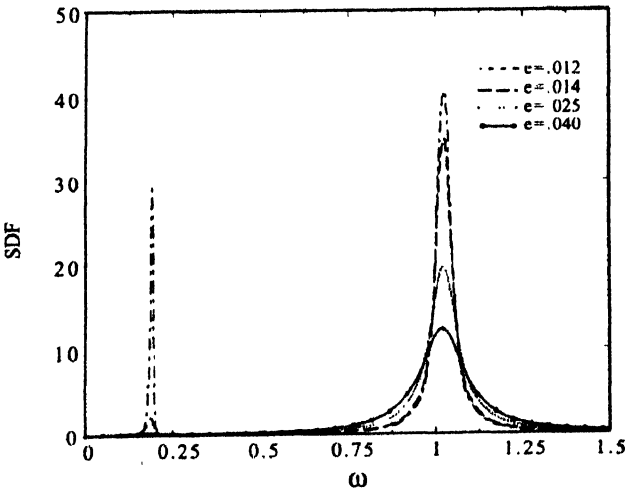

Figure 6. Plot of SDF for fixed values of $s = 0.151$, $z = 0.052124$, $p = 0.5$ and $t = 0.03$ and for different values of $e = 0.012$, 0.014, 0.025, 0.04.

z = 0.05214 to 0.046 the excitation peak shown shift to lower frequency and broadening with decrease of peak intensity. This shift to the low frequency side corresponds to a decrease of the SC gap.

The effect of q = 0 phonon frequency ω_0 on the SC gap excitation mode is shown in Figure 5. When the bare phonon frequency (p) of the system increases, the SC gap modes are renormalized to low valueds and hence shift to low frequencies. For $p \simeq 1$ the SC gap excitation is suppressed completely.

We have extended the theory to include the life time broadeing for thebare phonon in the form of $e = \eta/\omega_D$. The effect of e on the Raman excitation peaks is shown in Figure 6. As expected the SC gap excitation peak shows a large broadening with rapid decrease of spectral height with no shift in the position of the peak. When the spectral width e is increased for a high $e \simeq 0.04$ the SC gap excitation is completely suppressed.

6. Conclusion

We have considered a normal electron-phonon type coupling in a CDW superconductor where the CDW-AM phonon mode is coupled to the SC gap. This SC gap mode appears in the Raman spectra. The electron-phonon coupling from $s \simeq 0.10$ to 0.15 shows the SC gap mode for the CDW material in the Raman spectra. For $s < 0.10$ the SC excitation desappears at temperature $t \simeq 0.03$. The increase of temperature broadens the peak with decrease of spectral height. The decrease in the SC gap excitaion frequency to low values in the CDW·superconducting material. The increase of the bare phonon frequency of the CDW material suppresses the spectral height and shifts its renormalized frequency to low values. The increase in life time broadening of the phonon frequency also broadens the peak corresponding to the superconducting gap mode.

Acknowledgment

Two of the authors (BP and GCR) gracefully acknowledge the research facilities offered by the Institute of Physics, Bhubaneswar during their short stay.

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